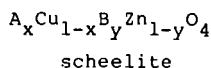
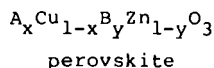


CRYSTAL AND CATALYTIC CHEMISTRY OF METHANOL SYNTHESIS

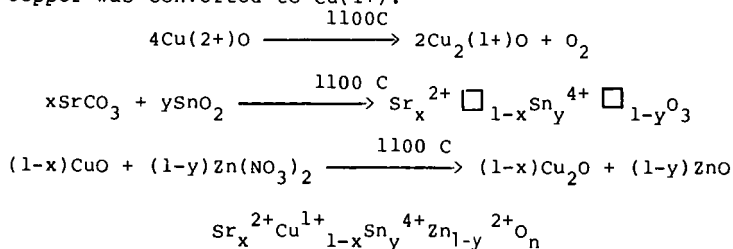
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Solid solutions of mixed metal oxides in the perovskite (ABO_3) and scheelite (ABO_4) families of crystals were used as host materials for the preparation of methanol synthesis catalysts. These materials contain a partial substitution of a copper (1+) ion in the A-sites of their structures and a Zn(2+) ion in their B-sites as homogeneous solid solutions in a host lattice containing at least two other metal oxides.



The synthesis of these unusual materials was accomplished by recognizing that copper oxides exist as an equilibrium mixture of Cu(1+) and Cu(2+) ions at temperatures in the range of 1100 C in air. Utilizing high temperature synthesis techniques, copper was disproportionated to a mixture of copper(2+) and copper(1+) oxides under oxidizing conditions. When this equilibrium mixture was exposed at high temperatures to a metal oxide composition containing a substoichiometric amount of the A-site cation, the equilibrium was shifted to copper(1+) which was incorporated into the A-site of the host. Due to the removal of Cu(1+) from the equilibrating system by its location in the stable A-site, all of the copper was converted to Cu(1+).



Support for the structure for these compounds was gained from an analysis of their magnetic susceptibility data, photoelectron spectra, x-ray diffraction data, and analytical analysis. The compounds were shown by the magnetic susceptibility data to be diamagnetic which was consistent with a d-10 copper(1+) ion. The absence of any shake-up structure in their ESCA spectra was

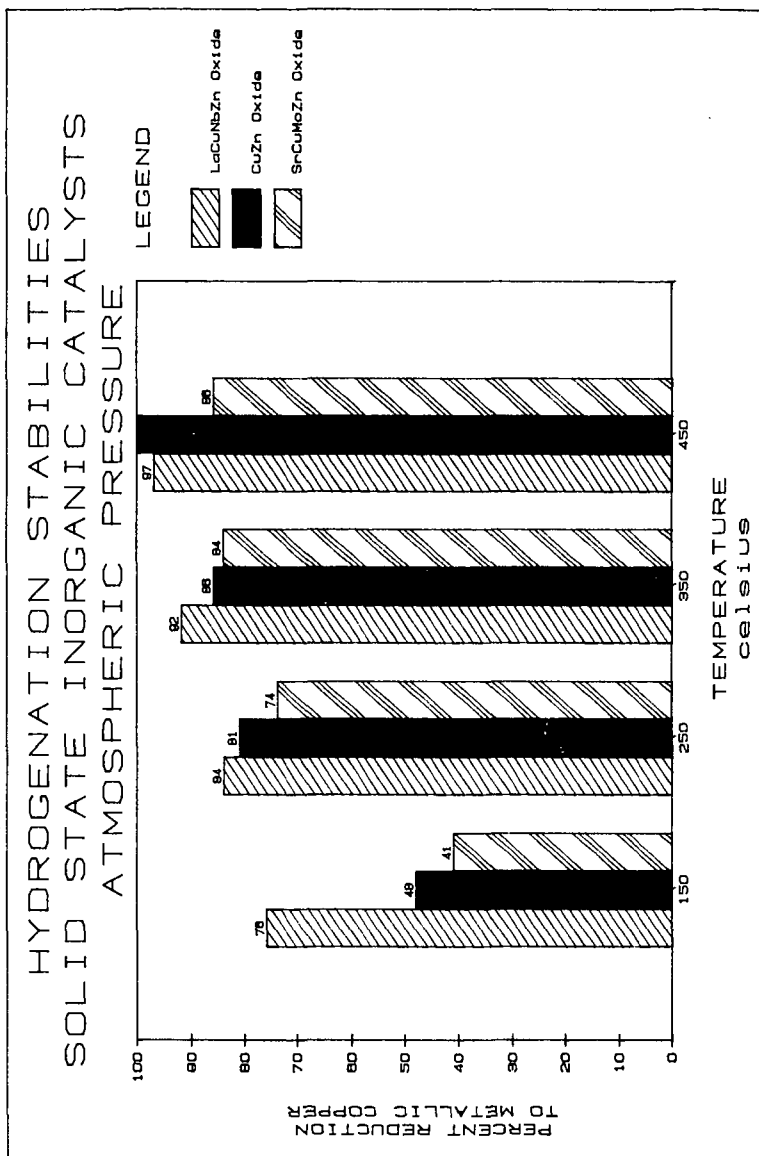
consistent only with a copper (1+) ion incorporated in the A-site of the solid state mixed metal oxide. Copper (2+) ions demonstrated large shakeup satellites in their ESCA spectra.

The objective of the synthesis of these novel materials was to provide a homogeneous solid solution of both the copper(1+) and zinc(2+) ions in the lattices of metal oxides which have unusual thermal and structural stability under reducing conditions. Using these materials which were then further modified by other ions substituted in the A- or B-sites, gradual electronic changes may be made in the copper(1+) ion. The solid solution, ion modified compounds will be subsequently used to understand the activation of carbon monoxide in methanol synthesis.

The activities of these materials as methanol synthesis catalysts were studied at 75 atm. and 230 C. The stabilities of the copper(1+) ions in the host lattices were examined between 200 C to 450 C in separate studies using diluted hydrogen in nitrogen. The methanol synthesis activities of these compounds when compared on a unit surface area basis were generally a bit lower than the copper modified zinc oxide catalysts prepared by coprecipitation. Their surface areas were substantially smaller than the Cu-Zn-O catalyst. In only a few cases was the stability of these solid state solutions toward reduction to copper(0) superior to that of the copper modified zinc oxide catalyst. This finding was surprising since one would expect the Cu(1+) atom of about 0.96 atomic radius to be configurationally stable from purely structural considerations. However, location of the mono-cation in a substantially greater electronegative lattice position contrasted to its solution in pure ZnO, may account for the observation of accelerated reduction in most examples using the complex solid state inorganics. A comparison of the relative rates of reduction of the solid state inorganic solutions to the coprecipitated standard Cu-Zn-O catalyst is shown in Figure 1. These data show that the metal ion composition may be used to regulate stability.

A study of the ease of reduction to metallic copper in a series of 10% metal ion modified copper zinc (25%/65%) oxide catalysts was performed. In addition a newly developed attrition test was used to examine the attrition resistance of these catalysts to mechanical wear. Ten percent concentrations of lanthanum, aluminum, magnesium, strontium, zirconium, tin, tungsten, molybdenum and chromium oxides were prepared with 25% copper oxide and 65% zinc oxide by coprecipitation. These modified compositions were found to be of superior mechanical strength when compared to unmodified 30% copper oxide-70% zinc oxide. In most cases the unmodified catalyst was reduced in hydrogen more easily than the modified ones. The solid state inorganic solutions of copper in the perovskite or scheelite crystals classes were substantially more attrition resistant than the modified copper zinc oxide systems.

FIGURE 1 RELATIVE DEGREES OF REDUCTION OF
 $\text{La}_{.8}\text{Cu}_{.2}\text{Nb}_{.8}\text{Zn}_{.2}\text{O}_{3.5}$, $\text{Cu}_{.73}\text{Zn}_{.27}\text{O}_x$, and $\text{Sr}_{.8}\text{Cu}_{.2}\text{Mo}_{.8}\text{Zn}_{.2}\text{O}_{3.5}$
 to copper zero at temperatures of 150°C to 450°C by 2% hydrogen in nitrogen
 at a gas hourly space velocity (GHSV) of 3500 hr^{-1} .



POSSIBLE RELATIONSHIPS OF SITES FOR CO ADSORPTION WITH METHANOL SYNTHESIS ACTIVITY OF SUPPORTED Pd CATALYSTS

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Pd/SiO₂ catalysts with and without promoters for methanol synthesis have been previously studied (1-6), with partially contradictory conclusions. Lunsford, et al. (3), concluded that Pd structural effects play an important role in the activity of the catalyst, since catalysts with small Pd crystallites produce methanol while larger crystallites produce methane. Such structural effects can be induced by different grades of silica support. On the other hand, Ponec, et al. (1,6) believe that electronic factors are more important and Pd II "ions" are the centers for CO activation. The number of such sites is presumably increased by the presence of alkali metals. The effect of alkali metals such as Li appears to be more complex (1,5). Whatever the nature of the active centers, the addition of basic metals as well as the use of basic supports (4) promotes reactivity.

EXPERIMENTAL

The reactor used in testing the methanol synthesis catalyst was a vertical 1/2" stainless steel tube enclosed in a hinged furnace. Cylinder CO and H₂ were fed into the system via pressure regulators and Brook's mass flow controllers. The desired pressure was maintained at the reactor outlet by a pneumatically operated research control valve. Outlet flows were measured by a wet test meter.

Four grams of vacuum-dried catalyst (14-20 mesh) were diluted (if necessary) to a 10 cc volume with α -alumina particles and placed centrally in the reactor. The catalyst was pretreated in situ by passing N₂ at 150°C for 30 minutes, and then passing H₂ at 340°C for 1 hour. Activities were measured after two hours running in a H₂/CO feed of mole ratio 2/1.

Infrared analysis were performed on a computerized IR Beckman 4260 as previously described (7). Corrections were applied for changes in background bands (arising from the support) caused by cooling of the sample when CO was admitted to the cell. Some spectra were recorded with a Perkin-Elmer 1550 FTIR spectrometer.

The catalysts were prepared using two different batches of Davison silica gel, 57 and 59.

Impregnated catalysts were prepared by the incipient wetness technique. Pd ion exchanged catalysts were prepared by the following procedure: The required amount of Pd (NH₃)₄(NO₃)₂ solution was added to a slurry of the mixture gel and water. The water was alkalinized by adding a few drops of NH₄OH to make the pH ~9.5. After mixing for 1 hour, the silica was washed and filtered and, finally, calcined at 300°C for 2 hours. For the Li doped samples, Li was added as the hydroxide prior to the Pd impregnations.

RESULTS AND DISCUSSION

Activity Measurements

The reproducibility of activity measurements by the reactor was tested and found to be about $\pm 20\%$ of the absolute value in terms of CO converted.

Some preliminary results on pretreatment variations indicated that the initial activity of the unreduced Pd catalysts was half that of the fully reduced catalyst, but that on increasing time on stream, the activity approached that of the fully pretreated catalyst.

Two different batches of Davison silica, #57 and #59, were used in preparing the catalysts. Although specifications for the two were the same, there were some differences in the results observed, as shown in Table I.

Table I. Variation in Silica Support
Conditions: 500 psig, SV = 900 hr⁻¹, 275°C
and H₂:CO = 68.2:31.8

Catalyst	Method of Pd Addition	% CO Converted to MeOH
5% Pd/SiO ₂ 57	Impregnated	0.8
5% Pd/SiO ₂ 59	with PdCl ₂ solution	2.5
5% Pd/SiO ₂ 57	Ion exchanged with	1.2
5% Pd/SiO ₂ 59	Pd(NH ₃) ₄ (NO ₃) ₂	3.0
5% Pd/1.6% Li/SiO ₂ 57	Impregnated with	4.6
5% Pd/1.6% Li/SiO ₂ 59	PdCl ₂ solution	6.0

In all cases, Davison 59 showed an increase in activity over Davison 57. However, the increase was smallest with the Li promoted catalyst, suggesting the differences in activity may arise out of differences in the amount of residual alkali metal contaminant.

Differences in the mode of adding Pd to the support evidently made little difference in the activity of the catalyst as shown by the data of Table II.

Table II. Variation in Pd Addition
Conditions: As in Table I

Catalyst	Method of Pd Addition	% CO Converted to MeOH
5% Pd/SiO ₂ 59	Impregnated with PdCl ₂	2.5
5% Pd/SiO ₂ 59	Impregnated with Pd(NO ₃) ₂	2.0
5% Pd/SiO ₂ 59	Ion Exchanged with Pd(NH ₃) ₄ (NO ₃) ₂	2.0
1.5% Pd/SiO ₂ 57	Impregnated with PdCl ₂	0.9
1.5% Pd/SiO ₂ 57	Impregnated with Pd(NO ₃) ₂	0.8

These data were obtained on catalysts ion-exchanged with amino nitrate complex or impregnated with either the nitrate or chloride salt.

Significant differences were observed when Li was added as a promoter.

Table III. Effect of Lithium Promotion
Conditions: As in Table I

Catalyst	Method of Pd Addition	% CO Converted to MeOH
5% Pd/SiO ₂ 57	Impregnated with	0.8
5% Pd/SiO ₂ 57 + 1.6% Li	PdCl ₂	4.6
5% Pd/SiO ₂ 59	Impregnated with	2.5
5% Pd/SiO ₂ 59 + 1.6% Li	PdCl ₂	6.0
5% Pd/SiO ₂ 59	Impregnated with	2.0
5% Pd/SiO ₂ 59 + 1.6% Li	Pd(NO ₃) ₂	5.0
1.5% Pd/SiO ₂ 59	Ion exchanged with	3.0
1.5% Pd/SiO ₂ 59 + 1.6% Li	Pd(NH ₃) ₄ (NO ₃) ₂	4.3

Table III shows that Li always increased the activity for every catalyst type used. The increase, however, was smallest for the Pd ion exchanged on silica 59 possibly since without Li this catalyst had a higher activity, but, also, this smaller increase could be a result of the absence of residual alkali in the support.

Infrared Spectra

Figures 1 to 5 represent IR spectra of CO adsorbed on some of the catalyst samples whose activities were measured in attempting to relate catalyst performance to catalyst surface properties. Each spectrum is characterized by bands near 2075 and 1975 cm^{-1} corresponding to weakly-held CO previously assigned to linear and bridged bonding of CO on Pd, respectively (8). The spectra after evacuation and therefore representing strongly held CO, typically show less intense bands near 2060 and 1900 cm^{-1} , again reflecting linear and bridged CO. Additional bands can also be seen. These probably reflect various bridged CO species held on different crystal faces (8).

Figures 1 and 2 show spectra of CO on 5% Pd/SiO₂ made by impregnation of the chloride and nitrate salt respectively. Although the general features are similar, some differences are observed in relative intensities of the bands near 2075 and 1975 cm^{-1} corresponding to a weakly-held linear and bridge bonded CO. Differences can also be seen in the frequencies of bands caused by strongly-held CO remaining after evacuation. No difference was observed in the relative activities of the two catalysts, however.

Figure 3 shows spectra of CO on 1.5% Pd/SiO₂ (ex. PdCl₂) which was run on the FTIR. This was the only case where a band at 2165 cm^{-1} was detected.

Figure 4 shows the effect of Li on the CO/Pd spectra obtained for 1.5% Pd ion-exchanged on Davison 59 silica. (Note change in absorbance scale.) The spectrum of CO on the catalyst shows significant differences from those on the impregnated catalysts. A much more intense linear CO band is observed and a relatively weaker bridge-bonded CO band. No difference is seen in the linear CO bands (2060 and 2090 cm^{-1}) when Li is present. Only a slight difference exists between the bridged CO bands, yet a small increase in activity was noted. The strongly-held bridged CO bands in the 1850-1950 cm^{-1} appear to be progressively decreased in intensity and shifted to lower frequencies as Li content increases.

Figure 5 shows spectra of CO on the catalysts of Figures 1 and 2, respectively, after the addition of Li. Comparison with Figures 1 and 2 shows very little effect of Li on the CO spectra in the region above 1950 cm^{-1} . In the region below 1950 cm^{-1} , however, there was a significant increase in both weakly and strongly held bridged CO. There was a large corresponding increase in activity, by factors of 6 and 3, respectively, when Li was present.

DISCUSSION

Spectra of CO on Pd have been thoroughly discussed elsewhere (9). It was initially hoped, and expected, that among the variety of different types of bands observed for CO adsorbed on silica-supported Pd some correlation would be found with methanol synthesis activity. No obvious correlation was, in fact, apparent. Some previous speculation appears to have been excluded by the evidence, however, and possible explanations for Li promotion can be offered.

Careful attention was paid to possible adsorption of CO on Pd²⁺ ions, which would have been expected to give bands above 2100 cm^{-1} , and even, by analogy with Ni²⁺, as high as 2195 cm^{-1} (9). A band suggestive of Pd²⁺ adsorption sites was seen in only one instance. This was observed with the 1.5% Pd/SiO₂ (ex. PdCl₂) sample (Figure 3). After prereduction at 300°C and addition of CO, this catalyst showed a

very weak band at 2165 cm^{-1} which probably reflects CO held on Pd^{2+} ions. This catalyst was, however, one of the least active (see Table II). Unreduced Pd would not be expected under reaction conditions in any case, but the fact that activity was found to increase with increasing prereduction of the catalysts and, initially, with increasing time on stream strongly argues that Pd^{2+} sites are not, as postulated by Ponec, et al. (2,6), the active sites.

The infrared spectra show that Li addition has a small but definite effect on the bridged bonding of CO to Pd. Such bonding presumably occurs mainly on exposed faces of Pd crystallites. The effect could be either electronic or structural in nature. The Li, in a partial overlayer on a Pd surface, could affect the electronic properties of adjacent Pd atoms, changing their subsequent adsorption of CO. Alternatively, Li might promote exposure of crystal faces different from those normally present. The existence of an effect of Li on bridge bonding of CO does not, of course, mean that this is the factor responsible for activity promotion by Li. The data generally show no obvious correlation of activity with any particular type of CO bonding as revealed by the frequency and intensity of infrared bands arising from adsorbed CO.

The fact that wide differences in the types of CO adsorption on reduced Pd made so little difference in catalyst activity while marked differences in activity were observed on catalysts with generally similar CO adsorption sites suggests that some factor other than CO binding could well be of major importance. This could be the ability of the support to heterolytically dissociate hydrogen to form hydroxyl and hydride species on the surface. Zinc oxide is well-known for its ability to do this and evidence has also been presented that MgO and La_2O_3 can similarly dissociate hydrogen. Work in this laboratory has shown that alumina possesses a few sites which exhibit this behavior. The ability to form surface hydride may be the essential feature needed for methanol synthesis in addition to the non-dissociative adsorption of CO. The effect of Li may be to provide surface sites on silica on which such dissociation can occur more readily. Further work is planned to investigate these possibilities. Obviously, the types of sites available for CO and H_2 adsorption under reaction conditions may differ from those seen on fresh or used catalysts. In situ IR studies under reaction conditions could shed additional light on this subject. Such studies are also planned.

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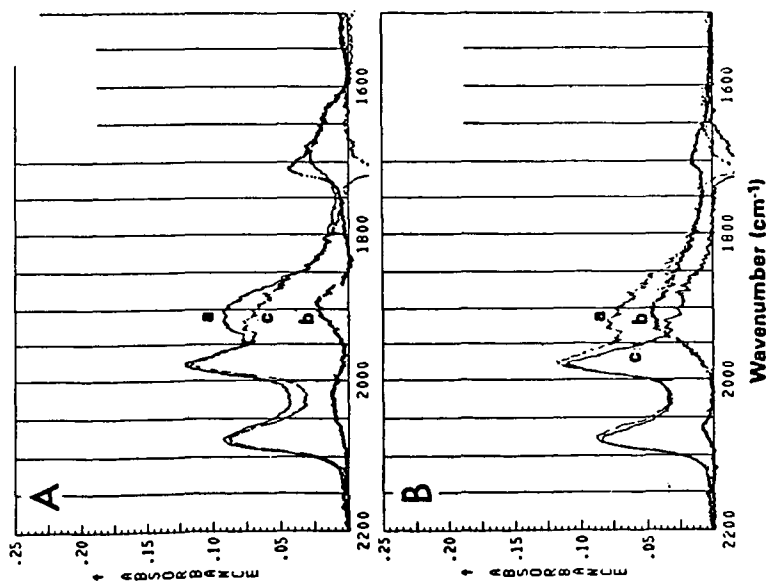


Figure 1. Spectra of CO adsorbed on 57 Pd/division 57 silica (ex PdCl_2).
 A. Spectra showing "cooling" correction
 a) CO (2.3 Torr); b) H_2 ; c) (a-b)
 B. Spectra showing strongly and weakly-held CO.
 a) "corrected" CO spectrum = C above
 b) CO held after 5 min. equiv. c, (a-b) = weakly-held CO.

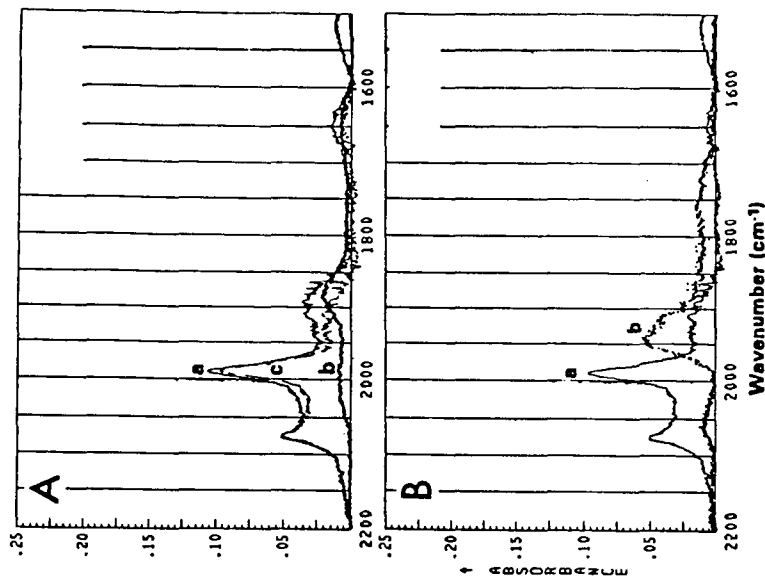


Figure 2. Spectra of CO adsorbed on 51 Pd/division 59 silica (ex $\text{Pd(WO}_3)_2$).
 A. Spectra showing "cooling" correction
 a) CO (2.3 Torr); b) H_2 ; c) (a-b)
 B. Spectra showing strongly and weakly-held CO
 a) weakly-held CO; b) strongly-held CO

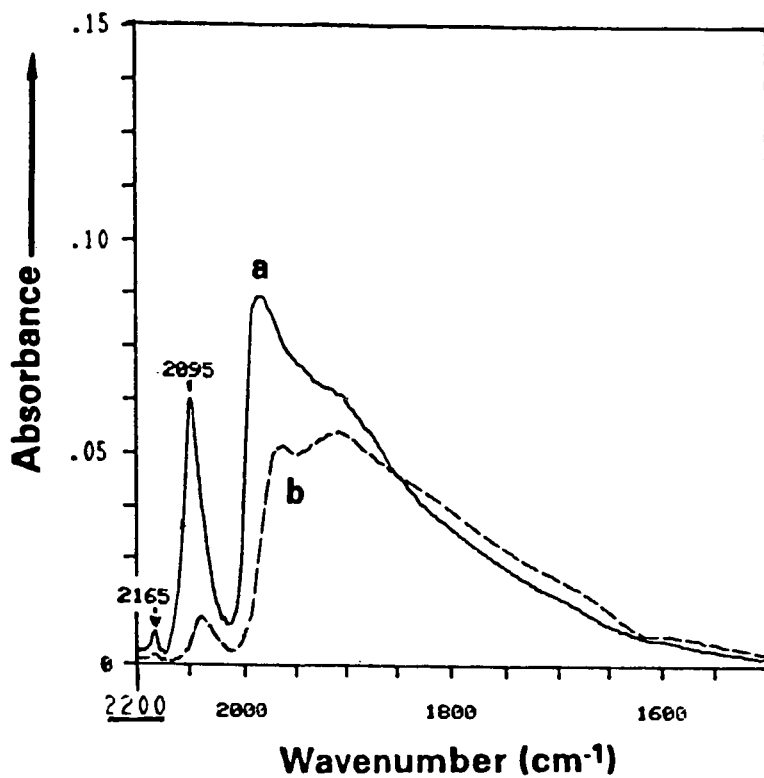


Figure 3. FTIR Spectrum of CO Adsorbed on 1.5% Pd/Davison 57 silica (ex PdCl_2)
A. CO (2.0 Torr);
B. After 5 min. evacuation.

(The background was subtracted, but no corrections were applied.)

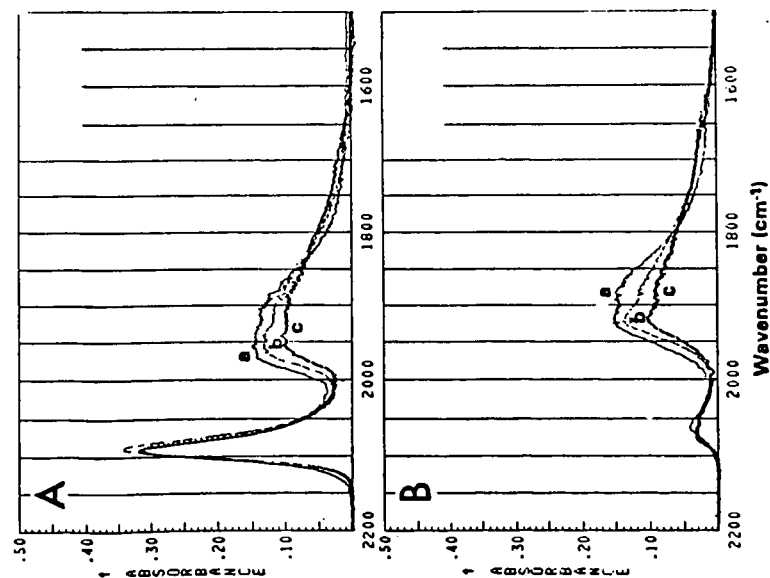


Figure 4. Effects of Li on 1.5% Pd/Devisom 59 silica (ion exchanged)
 A. Spectra of CO (2.1 Torr-corrected for "cooling") on catalysts containing the following Li contents:
 a) 0%; b) 0.7%; c) 1.0%
 B. Spectra of CO retained after 5 min. evacuation on the same catalysts (a, b and c above).

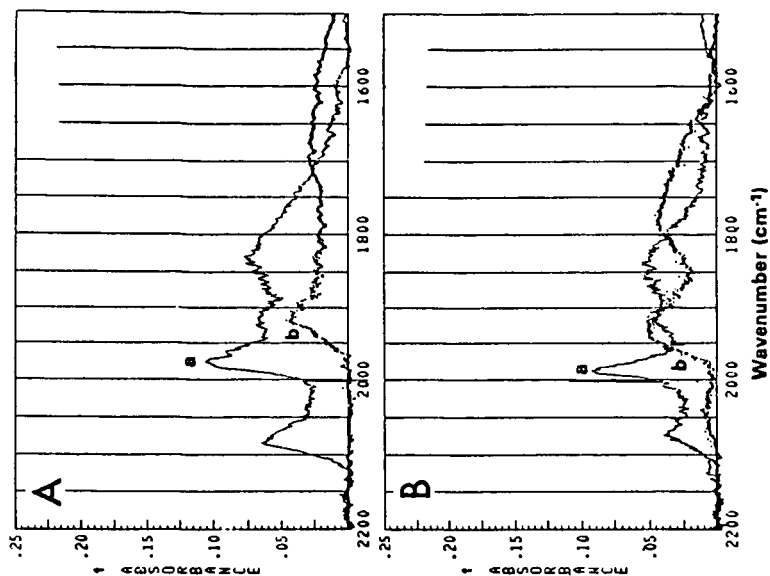


Figure 5. Effects of Li on 5% Pd/SiO₂
 A. CO/5% Pd/1.6% Li/SiO₂
 a) CO (2.2 Torr-corrected); b) after 5 min. evacuation.
 B. CO/5% Pd/1.6% Li/SiO₂
 a) CO (2.1 Torr-corrected); b) after 5 min. evacuation.

THE EFFECT OF ALKALI PROMOTION ON ALCOHOL SYNTHESIS OVER Rh/TiO₂

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I. INTRODUCTION

The importance of the direct synthesis of higher (C₂-C₆) alcohols from synthesis gas as a promising route for providing clean fuels and petrochemical feedstocks is generally recognized. It is known that the addition of alkali salts to methanol synthesis catalysts often results in greater yields of higher alcohols. However, little is known about how various alkali species affect the catalyst component and alcohol synthesis reaction. Rh catalysts are simple yet model systems for studying the effect of alkali promoters on CO hydrocondensation. Depending on the oxide support used, the product catalyzed by Rh may be primarily hydrocarbons or alcohols (1, 2). This paper reports on an investigation of the effect of various alkali species (Li, K, and Cs) on CO hydrocondensation over Rh/TiO₂. Rh/TiO₂ was an attractive catalyst to study since both hydrocarbons and oxygenated compounds are formed in significant quantities during CO hydrogenation. This provided the possibility to investigate simultaneously the effect of alkali promotion on the formation of these two types of products.

II. EXPERIMENTAL

The alkali-promoted rhodium catalysts were prepared by the impregnation of TiO₂ using RhCl₃·3H₂O and an alkali nitrate (Li, K, Cs) in aqueous solution having a pH of 3-3.5. The catalysts were prepared in such a way so that the Rh loading was 3 wt% and the atom ratio of alkali promoter to Rh was 1/2. After impregnation, the samples were dried overnight in air at 40°C and reduced in flowing H₂ on heating in 50°C steps (30 min.) to 400°C and holding for 16 hr. Prior to reaction, the TiO₂-supported catalysts were again reduced in flowing hydrogen at 500°C for 3 hr. to induce strong metal-support interaction (SMSI) (3). The study was carried out in a differential reactor at reaction conditions of 250-330°C, 10 atm, and CO/H₂=2. A small amount of ethylene (2.3 mole%) was added to the reactant mixture to study the specific reactions of this synthesis.

III. RESULTS AND DISCUSSION

The activity of CO conversion was observed to decrease in the order: unpromoted > Li > K > Cs. The rates of formation for all the products decreased upon alkali promotion but the oxygenate selectivities were enhanced as shown in Fig. 1. This clearly indicated that there was less suppression in the rate of oxygenate formation than in that of hydrocarbon formation. It may suggest that alkali promoters have a different effect on the formation of oxygenates than on that of hydrocarbons. The selectivity of acetone paralleled that of acetaldehyde suggesting that the acetone may be formed by the combination of the acetaldehyde intermediate and a surface methyl species as proposed by Schulz and Zein El Deen (4). The decrease in mole ratio of [MeCHO]/[EtOH] and (olefin)/(paraffin) as shown in Table I may be attributed to the suppression of hydrogenation as a result of alkali promotion. Hydrogenation suppression has been identified as a major

effect of alkali promoters on CO hydrogenation over transition metal catalysts (5, 6).

Although oxygenate selectivities were enhanced upon alkali promotion, the chain growth probability based on carbon number of both oxygenates and hydrocarbons was only increased slightly by alkali promotion. Less deviation of the ethylene fraction from the Schulz-Flory distribution was also observed on alkali-promoted catalysts, indicating that the effect of ethylene incorporation was less pronounced in the presence of alkali promoters.

In order to verify the above findings, a small amount of ethylene [2.3 mole %] was added to the reactant mixture. The results of ethylene addition are essentially consistent with the above findings.

IV. CONCLUSIONS

1. The rate of CO conversion decreased in the order: unpromoted > Li > K > Cs.
2. The hydrogenation ability also decreases in the order: unpromoted > Li > K > Cs.
3. The alkali promoters had different effects on the formation of oxygenates than on that of hydrocarbons.
4. The active sites for oxygenate formation during CO hydrogenation over Rh/TiO₂ appeared not to be sensitive to the chemical nature of the alkali promoter.

ACKNOWLEDGMENT

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TABLE I The Effect of Alkali Promoter on [MeCHO]/[EtOH]
and [olefin]/[paraffin] Ratios

	Rh/TiO ₂	Li-Rh/TiO ₂	K-Rh/TiO ₂	Cs-Rh/TiO ₂
$\frac{[\text{MeCHO}]}{[\text{EtOH}]}$	0.3	0.6	2.7	10.4
$\frac{[\text{C}_3\text{-C}_5\text{olefins}]}{[\text{C}_3\text{-C}_5\text{ paraffins}]}$	2.7	5.8	4.6	4.2

Reaction conditions: CO/H₂ = 2, 300°C, 10 atm

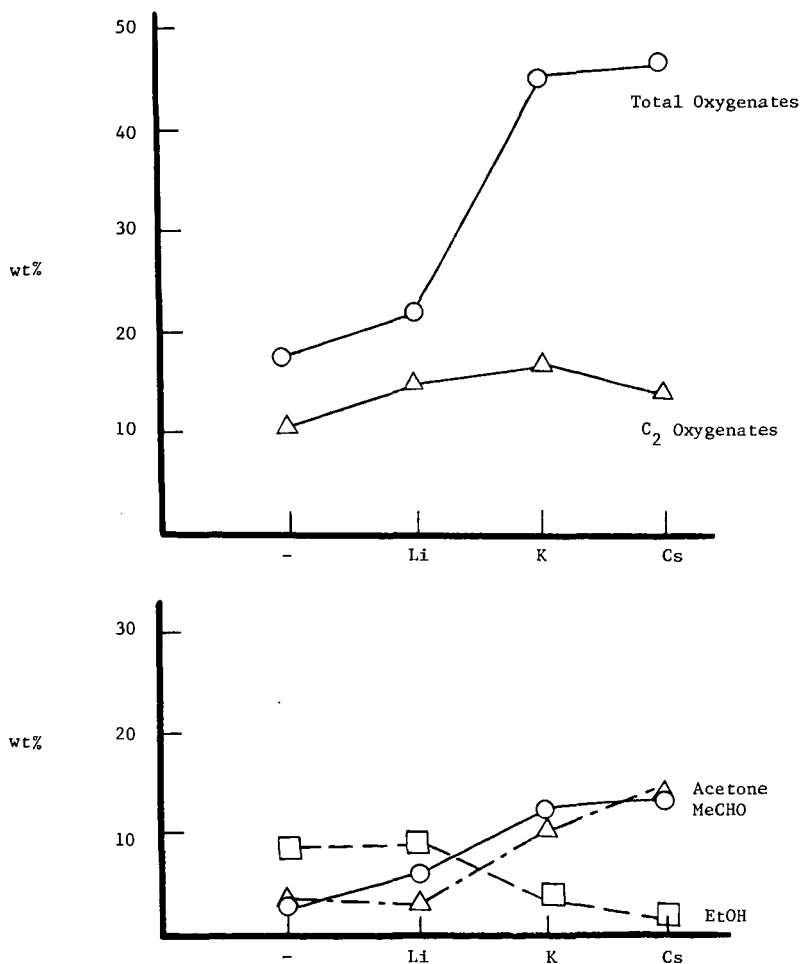


Figure 1: The Effect of Alkali Promotion on Oxygenate Selectivity for Rh/TiO₂ (CO/H₂ = 2, 300°C, 10 atm)

Heteropoly Compounds and Their Properties as Catalysts, in Oxidation Reactions and Methanol to Hydrocarbon Process.

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INTRODUCTION

Heteropoly compounds are ionic solids with complex, high molecular weight anions, the latter possessing a minimum of three elements. Although heteropoly compounds possess a variety of structures, those of interest in the present work have anions with cage-like structures, often referred to as Keggin units (Fig. 1). These have a central metal atom contained within a tetrahedron of oxygen atoms which is itself surrounded by twelve octahedra of oxygen atoms with a second metal atom at each of their centres. The octahedra overlap and share a portion of their oxygen atoms with each other and with those of the central tetrahedron. The central metal atom is typically P, Si, As, while the peripheral metal atoms are commonly W, Mo, V, and Ti.

Fortunately, detailed structural information for some of the heteropoly compounds is beginning to become available. One of the most detailed studies was that performed by Brown, Noe-Spirlet, Busing and Levy (1) with X-ray crystallography and neutron diffraction on 12-tungstophosphoric acid ($H_3PW_{12}O_{40} \cdot nH_2O$). Their work showed that the proton in this heteropoly acid is surrounded by four water molecules only two of which are hydrogen-bonded to the proton at a given time. The water molecules are, in turn, hydrogen-bonded through their hydrogen atoms to the outer or terminal oxygen atoms of the anions (Fig. 2).

Heteropoly compounds have gained increasing interest in the last few years, largely as heterogeneous catalysts, but also in homogeneous catalysis (for example, refs. 2-6). One of the sources of the interest in the catalytic properties of these solids undoubtedly lies in their multifunctional capabilities. As a result of variation in their elemental composition, virtually a continuous change in catalytic functions can be achieved, ranging from that associated with Bronsted acidity to that with oxidation catalysis, while the Keggin structure is retained.

While the cation can be shown to influence the catalytic properties in various ways, but principally through changes in both the bulk and surface properties of the heteropoly compound, the present work is primarily concerned with the effect of the anion on the bulk, surface and catalytic properties of heteropoly compounds. The influence of the anion, and in particular the nature of both the central heteroatom and the peripheral metal atoms, can be seen from the results of a variety of experiments. Hayashi and Moffat (2) have shown that 12-tungstophosphoric acid catalyzes the gas phase conversion of methanol to hydrocarbons at 350°C, for example, while with 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$), oxidation predominates. Pretreatment of the former catalyst with air at 400°C reduces the conversion to hydrocarbons, while the use of helium or hydrogen in the calcination is beneficial to the conversion process.

The dehydration of propanol is catalyzed by a variety of heteropoly acids as $H_3PW_{12}O_{40}$ $H_4SiW_{12}O_{40}$ $H_5PW_{10}V_2O_{40}$ $H_3PMo_{12}O_{40}$ $H_5PMo_{10}V_2O_{40}$ $H_4SiMo_{12}O_{40}$

(5). In the oxidation of methacrolein heteropoly acids $H_3PMo_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$ have been shown to be more active and selective than $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ (6). In the oxidation of acrolein, methacrolein, and isobutyric acid by $H_3PW_xMo_{12-x}O_{40}$, the conversion increases as the value of x decreases, that is as the molybdenum content increases (6). Finally it should be noted that in many of the reactions catalyzed by heteropoly compounds, the existence of the Keggin structure of the anion appears to be a necessary although not a sufficient condition for the efficacy of the heteropoly compounds as heterogeneous catalysts (7).

Although the anion structure and composition are quite evidently of particular importance to the activity of the heteropoly compounds, the nature of the cations cannot be disregarded. Hayashi and Moffat (3) have compared the activity and selectivity of a number of salts of 12-tungstophosphoric acid in the conversion of methanol to hydrocarbons. Of the metal salts employed, Na, Zr, Zn, B, Mg, and Al, the first and the last produced the lowest and highest yields, respectively, of hydrocarbons. The yield of hydrocarbons was shown to increase with decreasing magnitude of charge on the peripheral oxygen atoms of the anion. The ammonium salt of 12-tungstophosphoric acid was found by Hayashi and Moffat (4) to produce significantly higher yields of paraffinic hydrocarbons, as contrasted with the largely olefinic products from both the parent acid and its metal salts.

In the present paper the results from temperature programmed desorption (TPD), photoacoustic spectroscopy in the infrared region (PAS), and semi-empirical (extended Hückel) calculations are presented to demonstrate the relationship between the cation, the anion and catalytic properties of the heteropoly compounds.

METHODS

To conserve space only the briefest description of procedures will be presented. The TPD experiments were carried out on a standard apparatus, described elsewhere (8,9). Both a thermal conductivity detector and a C.E.C. mass spectrometer, the latter attached to the system via a variable leak valve, were used as detectors. PAS-FTIR spectra from 4000-550 cm^{-1} were recorded at 5 cm^{-1} resolution on a Bomem DA3.02 Fourier Transform global source and KBr beamsplitter. The photoacoustic detector module, supplied as a standard accessory by the manufacturer, was used with minor modifications (10).

RESULTS AND DISCUSSION

The TPD of 12-tungstophosphoric acid exhibits two peaks (Fig. 3), one centred at 473°K (Peak 1) with an unresolved shoulder on the high temperature side, the other a very broad asymmetrical peak centred around 773°K (Peak 2), both due entirely to water as shown from mass spectrometry. The magnitudes of peaks 1 and 2 corresponded to 1.3-1.4 and 6.5 water molecules per Keggin Unit (KU), respectively. Outgassing at 463 or 593°K essentially removed peak 1 but had no effect on peak 2. No peaks were observed after outgassing at 723°K. It should be noted that copious quantities of water were evolved from the untreated HPW at room temperature when a stream of helium was passed through the sample. Water desorbed during outgassing at 463 or 593°K could be replaced by contacting the acid with water vapour at 298°K, but after outgassing at 723°K it was not possible to restore the original TPD behaviour.

The heteropoly acids, 12-molybdophosphoric acid and 12-tungstosilicic acid, as with HPW, displayed two peaks (1 and 2) both due to water (not shown). In addition a very sharp peak (peak 3) was evident on the high temperature side of

peak 2. While the positions of the peaks for HSiW were similar to those with HPW, those for HPMo were found at approximately 373, 673, and 723°K, for peaks 1, 2, and 3, respectively. The importance of the peripheral metallic element of the anion in determining the TPD behaviour is evident.

The position of peak 1 for each of the acids reported here is consistent with the type of multiple hydrogen bonding interactions between the acid and molecular water, as found by Brown et al (1). Since the position of peak 1 depended strongly on the peripheral element of the anion, it appears that such interactions occur externally to the Keggin Unit, consequently largely shielded from influence by the central atom of the anion. It appears the peak 2 must be associated with a deprotonation of the catalyst, the protons combining with anionic oxygen to emerge as molecular water. X-ray diffraction analysis of HPW, which had been pretreated at 723°K suggested that decomposition of the structure had not occurred, in spite of the loss of anionic oxygen.

The PAS spectrum of HPW after pumping at room temperature displays a featureless background absorption which extends across the range from approximately 2000 to 4000 cm^{-1} (Fig. 4). The broad band at 3200 cm^{-1} and the more intense and narrow band at 1710 cm^{-1} may be attributed to molecular water and protonated water. The bands below 1100 cm^{-1} are characteristic of the Keggin Unit. After heating with evacuation at various temperatures up to 450°C, the band at 1710 cm^{-1} decreases and shifts to 1640 cm^{-1} , the bending vibration of lattice water. The band at 1080 cm^{-1} is assigned to the triply-degenerate asymmetric stretching vibration of the central phosphate tetrahedron, while that at 980 cm^{-1} may be attributed to a stretching vibration of the bonds between tungsten and the outer oxygen atoms. Although at 450°C bands associated with the anion structure have diminished somewhat in intensity it is apparent that the structure remains essentially intact.

The twelve octahedra surrounding the central tetrahedron in the Keggin unit can be divided into four compact tritungstate groups, $\text{W}_3\text{O}_3^{8-}$, resulting from the edge sharing of three WO_6 octahedra (11) (Fig. 5b). The three octahedra in each such group have one common oxygen atom, which is also part of the inner tetrahedron in the heteropoly anion, and three other oxygen atoms are each shared by two octahedra to form the edge-shared unit. In $\text{W}_3\text{O}_{13}^{8-}$ there are three terminal and three bridging oxygen atoms on the outer surface of the unit, when viewed as a fragment of the heteropoly anion. The central tetrahedron may then be attached to produce the $\text{XM}_3\text{O}_{16}^{n-}$ species (Fig. 5a), where X refers to the central atom and M the peripheral metal atom. The use of this fragment to simulate the heteropoly anion in semi-empirical extended Hückel calculations provided a convenient means of evaluating the effect of charges in both the central and the peripheral atom.

The effect of changes in the central atom and the peripheral atoms of the Keggin structure may be observed from calculations on $\text{PW}_3\text{O}_{16}^{9-}$ (PW), $\text{SiW}_3\text{O}_{16}^{10-}$ (SiW) and $\text{PMo}_3\text{O}_{16}^{9-}$ (PMo) (Fig. 6). The net atomic charges on the outer atoms of the former two species are similar, while those on the fragment containing molybdenum are considerably more negative. In addition, the partitioned energies for the M-O (outer) bond on PW and SiW are approximately the same, that on PMo is considerably smaller. Evidently, a change in the central atom has little effect on either the atomic charges of the outer oxygen atoms or the partitioned energies of the bonds formed by these atoms with the peripheral metal atoms. In contrast, substitution of the peripheral atoms, with the central atom fixed, produces substantial changes in the two properties.

The results of these calculations together with the available experimental data are consistent with the conclusion that Bronsted acidity increases as the

magnitude of the negative charges on the outer oxygen atoms of the heteropoly fragment decreases, while the activity in oxidation reactions can be correlated with the energy associated with the bond between the outer oxygen atom and the peripheral metal atom.

It appears reasonable as a first approximation to assume that the protons in the heteropoly compounds are interacting primarily with the outer oxygen atoms of the anion structure. The acid strength, being directly dependent on the mobility of the protons, should then be inversely proportional to the magnitude of the negative charge on these oxygen atoms. In the oxidation processes involving heteropoly compounds, it may be reasonably assumed, again as a first approximation, that the activity of these catalysts is related to the ease with which the most immediately available oxygen atom can be removed from the anion. The partitioned energy of the bond associated with the peripheral metal atoms and the outer oxygen atoms of the anion would therefore appear to fill this role.

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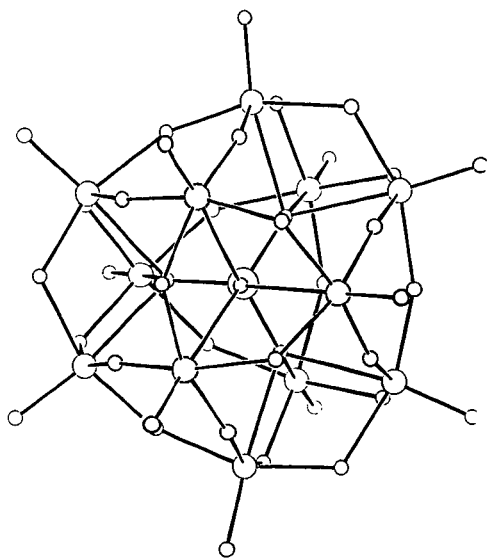


Figure 1 Anion of $\text{SiMo}_{12}\text{O}_{40}^{-4}$

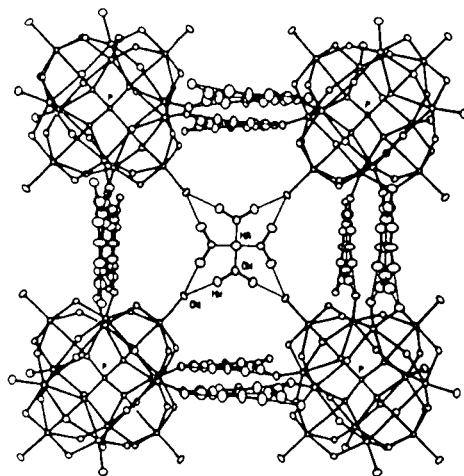


Figure 2 Arrangement of cations, water, and anions in 12-tungstophosphoric acid.

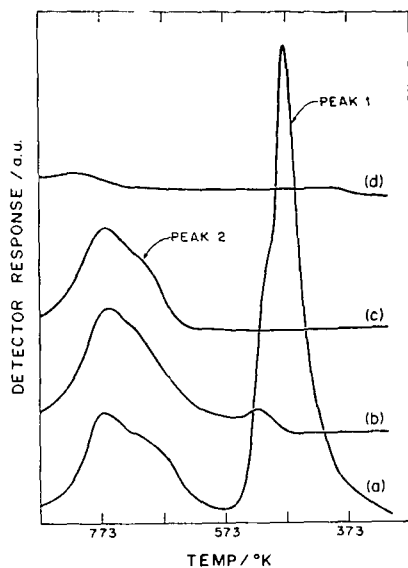


Figure 3 Temperature Programmed Desorption spectra of 12-tungstophosphoric acid after pretreatment temperatures of (a) 298 K, (b) 463 K, (c) 593 K, (d) 723 K (9).

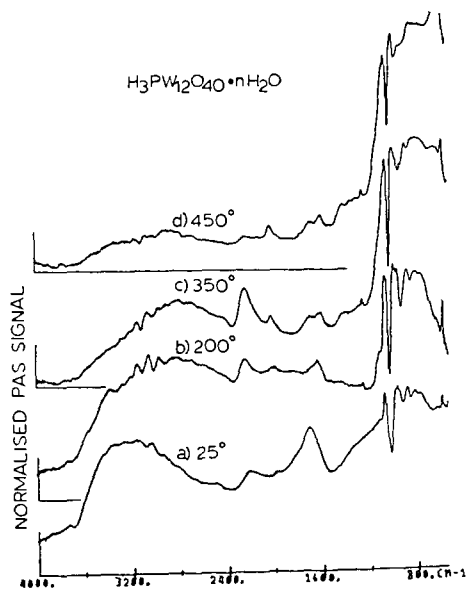


Figure 4 Photoacoustic spectra of 12-tungstophosphoric acid after heating with evacuation at various temperatures (10).

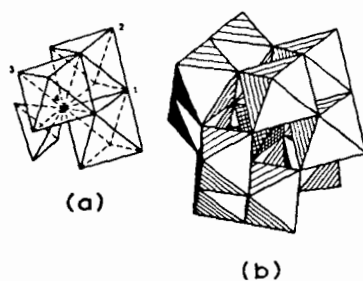


Figure 5 (a) Fragment $\text{XM}_3\text{O}_{16}^{m-}$ of heteropolyanion.
(b) Heteropolyanion showing position of fragment.

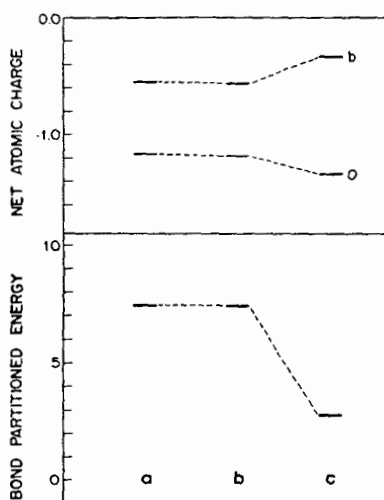


Figure 8 Results of extended Hückel calculations of net atomic charges on bridging (b) and outer (o) oxygen atoms and partitioned energies for the N-O (outer) bond.